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ARCHON Technical Reference and User Manual
ARCHON58

Russell A. Armstrong
Mission Research Corp
P.O. Box 7957
Nashua, NH 03060

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Technical Report

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Russell A. Armstrong

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13. ABSTRACT (*Maximum 200 words*)
This combined report on ARCHON58 is an update to the earlier report on ARCHON22 (DNA-TR-89-65-V1&2). The earlier report consisted of two volumes, volume 1 being a detailed description of ARCHON and the ARCHON reaction rate data set listing, and volume 2 being the user guide to ARCHON. There have been significant updates to both the ARCHON code and to the reaction rate data set. Updates to the ARCHON code itself has been primarily to address run time efficiencies and inadequacies in the former code - there is a speed-up factor of 20-50 with ARCHON58 over ARCHON22. This speed-up is primarily attributable to modifications to the integration technique and the addition of a user-specified option to substitute the GEAR integrator method. One of the more important changes is the addition of a variable time step routine which has been added so that when ARCHON senses a rapid change in a driver parameter (temperature, density, e.g. shock wave), the time step is reduced accordingly. The "standard" ARCHON reaction rate data set is now called ARD_5.set and has been significantly updated. It now consists of over 9000 reactions involving over 400 species. Several corrections have been made to the original ARCHON file and significant additions have been made in electron impact dissociation and ionization and in molecular nitrogen electronic excitation to the "A", "B" and "C" states of the neutral and the "A" and the "B" states of the ion. Additions have also been made in the area of negative ion and electron-impact reaction rates.

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PREFACE

The ARCHON family of codes represents a portable and flexible first-principles chemical physics kinetics code. It is designed as a "numerical testbed" to augment or benchmark existing codes and to serve as a first-principles chemistry code for new applications. ARCHON is written in ANSI-standard "FORTRAN-77" language, with great emphasis placed on portability of the code. The code has recently been successfully compiled in optimized FORTRAN90.

This combined report on ARCHON58 is an update to the earlier report on ARCHON22 (DNA-TR-89-65-V1&2. The earlier report consisted of two volumes, volume 1 being a detailed description of ARCHON and the ARCHON reaction rate data set listing, and volume 2 being the user guide to ARCHON. There have been significant updates to both the ARCHON code and to the reaction rate data set. Updates to the ARCHON code itself has been primarily to address run time efficiencies and inadequacies in the former code - there is a speed-up factor of 20-50 with ARCHON58 over ARCHON22. This speed-up is primarily attributable to modifications to the Taylor-series integrator and the addition of a user-specified option to substitute the GEAR integrator method. One of the more important changes is the addition of a variable time step routine which has been added so that when ARCHON senses a rapid change in a driver parameter (temperature, density, e.g. shock wave), the time step is reduced accordingly. Other changes are basically transparent to the user, except for the increase in speed.

The "standard" ARCHON reaction rate data set is now called ARD_5.set and has been significantly updated. It now consists of over 9000 reactions involving over 400 species. Several corrections have been made to the original ARCHON file and significant additions have been made in electron impact dissociation and ionization and in nitrogen electronic excitation to the "A", "B" and "C" states of the neutral and to the "A" and the "B" states of the ion. Additions have also been made in the area of negative ion and electron-impact reaction rates. However, *the user is cautioned* that in the area of negative ion chemistry, there is considerable uncertainty in the rates since there is a paucity of specific rate measurements on the topic. The reaction rate data set is heavily commented and should be treated as "experimental" in the sense that it is undergoing constant updates and revisions. Comments and suggestions for the reaction rate data set are welcome.

Requests for the code and data base should be addressed to:

Mission Research Corporation
ATTN: Dr. Russ Armstrong
One Tara Blvd, Suite 302
Nashua, NH 03062
tel: (603) 891-0070 x203.

Please state the organization you are with, the reason for the request and the sponsoring agency. This allows us to keep a record of users and application of the ARCHON code. Questions, comments and/or suggestions are encouraged and should be sent to Russ Armstrong, preferably via e-mail at rarmstrong@mrcnh.com.

CONVERSION TABLE

(This Conversion Table is Unclassified)

Conversion factors for U.S. Customary to metric (SI) units of measurement

MULTIPLY → BY → TO GET

TO GET ← BY ← DIVIDE

angstrom	1.000000 x E -10	meters (m)
atmosphere (normal)	1.01325 x E +2	kilo pascal (kPa)
bar	1.000000 x E +2	kilo pascal (kPa)
barn	1.000000 x E -28	meter^2 (m^2)
British thermal unit (thermochemical)	1.054350 x E +3	joule (J)
calorie (thermochemical)	4.184000	joule (J)
cal (thermochemical) /cm^2	4.184000 x E -2	mega joule/m^2 (MJ/m^2)
curie	3.700000 x E +1	*giga becquerel (GBq)
degree (angle)	1.745329 x E -2	radian (rad)
degree Fahrenheit	$t_K = (t_F + 459.67)/1.8$	degree kelvin (K)
electron volt	1.60219 x E -19	joule (J)
erg	1.000000 x E -7	joule (J)
erg/second	1.000000 x E -7	watt (W)
foot	3.048000 x E -1	meter (m)
foot-pound-force	1.355818	joule (J)
gallon (U.S. liquid)	3.785412 x E -3	meter^3(m^3)
inch	2.540000 x E -2	meter (m)
jerk	1.000000 x E +9	joule (J)
joule/kilogram (J/kg) (radiation dose absorbed)	1.000000	Gray (Gy)
kilotons	4.183	terajoules
kip (1000 lbf)	4.448222 x E +3	newton (N)
kip/inch^2 (ksi)	6.894757 x E +3	kilo pascal (kPa)
ktap	1.000000 x E +2	newton-second/m^2 (N-s/m^2)
micron	1.000000 x E -6	meter (m)
mil	2.540000 x E -5	meter (m)
mile (international)	1.609344 x E +3	meter (m)
ounce	2.834952 x E -2	kilogram (kg)
pound-force (lbs avoirdupois)	4.448222	newton (N)
pound-force inch	1.129848 x E -1	newton-meter (N-m)
pound-force/inch	1.751268 x E +2	newton/meter (N/m)
pound-force/foot^2	4.788026 x E -2	kilo pascal (kPa)
pound-force/inch^2 (psi)	6.894757	kilo pascal (kPa)
pound-mass (lbm avoirdupois)	4.535924 x E -1	kilogram (kg)
pound-mass-foot^2 (moment of inertia)	4.214011 x E -2	kilogram-meter^2 (kg-m^2)
pound-mass/foot^3	1.601846 x E +1	kilogram/meter^3(kg/m^3)
rad (radiation dose absorbed)	1.000000 x E -2	**Gray(Gy)
roentgen	2.579760 x E -4	coulomb/kilogram (C/kg)
shake	1.000000 x E -8	second(s)
slug	1.459390 x E +1	kilogram (kg)
torr (mm Hg, O° C)	1.333220 x E -1	kilo pascal (kPa)

*The becquerel (Bq) is the SI unit of radioactivity; 1 Bq = 1 event/s.

**The Gray (Gy) is the SI unit of absorbed radiation.

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SECTION 1
INTRODUCTION

At the start of FY87, MRC was tasked by (then) DNA/RAAE to develop ARCHON in support of specific NWE Chemistry R&D objectives. Key among those objectives was the establishment of a single updated, well-documented, and distributable code for support of chemical modeling within the (then) DNA NWE community and to the general atmospheric sciences community at large. However, it was deemed equally important that ARCHON be easily interfaced to systems-oriented and hydrodynamic codes such as SCENARIO, NORSE and MEGS, to augment their existing chemistry models and to support sensitivity and sufficiency analyses of their chemistry.

The ARCHON code is written in ANSI-standard "FORTRAN-77" language, with great emphasis placed on portability of the code. The code has been recently compiled successfully in optimized FORTRAN90. Without significant revision effort, ARCHON can be (and has been) run on machines ranging from PC's to a CRAY computer. Figure 1-1 conceptually illustrates the primary ARCHON objectives.

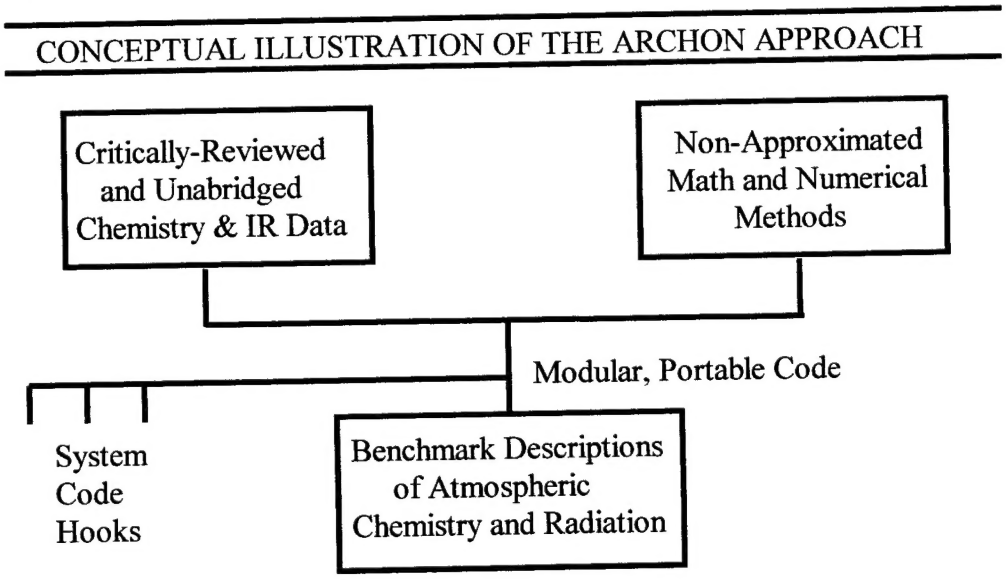

Figure 1-1. ARCHON conceptual objectives.

ARCHON is structured such that its chemistry is maintained in data bases independent of the executable code. This flexibility allows for any number of different applications to use the same code, with revisions to chemistry and physics taking place in the data bases. In addition, those data bases employ a highly non-constrained format that allows users great flexibility in defining and experimenting with problems. It is intended that ARCHON have the versatility and portability required to establish the code as a useful tool for diverse segments of the NWE community.

Although ARCHON provides a first principles treatment of chemistry, the initial intent of the code is not to replace existing chemistry codes with ARCHON, but to use this code as a numerical test-bed to aid in the analysis of important processes. The use of ARCHON-58 as a chemistry replacement may not make sense in many cases since its use could significantly increase computational time. ARCHON should be used to verify that chemistry modules in existing codes are operating properly and to analyze their chemistry content. Benchmarking with ARCHON allows the strengths and weaknesses of existing codes to be pinpointed and corrected. This allows for verification of a code without forsaking the speed of its present chemistry.

A specific example of how ARCHON can be helpful as a numerical testbed and analysis tool is in the area of validation of multidimensional hydrodynamics codes such as MEGS. Those codes attempt to minimize the amount of chemistry used, since the number of computational cells that they maintain is great. Replacement of their chemistry modules with ARCHON is not advisable, since the compute time required might be excessively long. However, ARCHON has been used to benchmark some few selected cells to assess the accuracy of the existing modules. By doing this type of testing, it is possible to determine whether important reactions are being omitted or if unnecessary reactions are being carried. This helps maintain the accuracy of the existing codes while also helping to improve their computational efficiency.

In addition to assessing and analyzing the small hydrodynamic code-coupled sets of chemistry in NWE codes, ARCHON can be applied to any chemical dynamics reaction set including general atmospheric investigations, combustion and polymer chemistry. The code has been used in investigations of stratospheric ozone, electrodynamic discharges above thunderstorms and jet engine combustion. ARCHON contains no specific constraints on the type of chemistry problem it can handle. A specific strength of ARCHON is that it can be employed to post-process the output of codes in order to describe the behavior of species which are minor relative to overall energetics but very important relative to optical, infrared, and radar impacts. ARCHON is structured so that it can be driven by pressure, temperature, and major species profiles which have been generated by or derived from the output of any other code.

The versatility of ARCHON allows the user to experiment with various reaction sets. Effects of the addition or omission of certain reactions can easily be examined by editing the database and re-running the problem. An ARCHON post-processor, DIG, is also available to analyze the chemistry sub-sets controlling user-specified species. This enables the user to initially include a large number of reactions in a problem description and then, through use of the DIG post-processor, determine which reactions can safely be removed. Extensions of this technique can be accomplished with Sensitivity Analysis tools, which have been developed but are not yet directly coupled to ARCHON.

This report is divided into five sections. Section 2 provides an overview of the code and data base architecture, a description of numerical integration method in ARCHON, and technical discussions of ARCHON applications. Section 3 includes a user manual for both ARCHON and DIG (the ARCHON post-processor). Section 4 provides specifics for ARCHON58 and DIG in the form of a user guide. The ARCHON reaction rate data set described in Section 5 is available as a companion to this report in the form of a floppy disk.

SECTION 2
ARCHON ARCHITECTURE

2.1 OVERVIEW DESCRIPTION.

ARCHON, a chemical kinetics computer code, has been developed to fill the need for a general-purpose first principles code which is capable of numerically integrating large, tightly coupled, unconstrained chemical kinetics problems. Unlike systems-oriented codes, ARCHON solves kinetics problems without resorting to simplifying assumptions intended for run time optimization. At present, ARCHON is not necessarily intended to replace the chemistry modules in systems-oriented codes, although it has been used that way. ARCHON primarily provides first principles validation and verification support to larger first-principles, engineering level and systems-oriented codes.

The purpose of this section is to discuss, in some detail, the architectural objectives guiding the development of ARCHON. The main objectives were ease of use, portability, modularity of the ARCHON source code, and maintenance of an open architecture.

The FORTRAN source code, called ARCHON, is a package of routines containing numerical methods as well as a variety of ancillary routines which support the numerical methods. The ancillary routines impress the physics of the particular scenario, (i.e. temperature, density, and ionization, changes etc.) on the chemical system. The chemical kinetics data used by ARCHON is incorporated in external data bases maintained independently of the source code. External data bases free the user from the tedious intervention required to update kinetic data bases contained in source code. A discussion of the maintenance, organization, and philosophy of the external data bases is provided later in this section.

ARCHON and its data bases were designed primarily for ease of use by a variety of users. The novice or occasional user can rely on the DSWA NWE data bases that ARCHON maintains, as well as calling on available user support at MRC/Nashua to successfully run problems. A more experienced user can quite easily write or modify the kinetics data bases to explore chemical kinetic systems of specific interest. The motivated user can use the flexibility inherent in ARCHON by running a variety of sensitivity studies searching for weaknesses (or strengths) in either user-supplied data bases or the DSWA NWE data bases. This last example illustrates the use of ARCHON as a numerical testbed.

ARCHON was written with expected wide distribution throughout the scientific modeling community whose members employ a variety of different computers and computational environments. Therefore, use of machine- and compiler-dependent extensions was purposefully avoided, facilitating portability to as wide a range of computational environments as possible. ARCHON was written in strict conformance to the 1978 ANSI-Standard definition of the FORTRAN language (i.e. FORTRAN-77). As noted

above, ARCHON also runs under FORTRAN90. Experience has shown that even with a well written code, utility and applicability can be diminished or thwarted if the code is written with machine- or compiler-dependent extensions which limit or preclude portability to different computing environments. ARCHON has been ported to and successfully run on a wide variety of machines ranging from the CRAY super-computers at Los Alamos to IBM PCs and their clones.

One of the major objectives was modular design of the ARCHON source code. Modular architecture requires that each functional task be confined to a clearly defined and written routine. Debugging, testing, updating, and adding new routines is eased by modular design, because possible adverse impacts on other working portions of the code are avoided.

The modular code structure and the principle of external data bases can be thought of as an open architecture. The philosophy of the ARCHON open architecture counters past popular doctrine called "information hiding" in structured programming. ARCHON was purposely written to make important variables globally available to each module of ARCHON and to the informed user as well. The implementation of open architecture in ARCHON accomplishes two important objectives: (1) it minimizes the number of globally important variables in general, and (2) it restricts the number of variables passed through the argument lists of the sub-programs in ARCHON.

Open architecture gives informed users the option to access important variables for inspection, modification, debugging, or use by routines calling ARCHON. Global variable availability provided by the ARCHON open architecture requires the interested user to be truly informed. As described here, open architecture can be abused through uninformed modification of variables by external routines or applications using ARCHON. This document is intended to convey the necessary information for confident exploitation of the open architecture in ARCHON.

Figure 2-1 illustrates the overall architecture of ARCHON. This diagram approximates the relationships between each functional block in the code. The actual flow of the program is somewhat more complicated than Figure 2-1 represents.

ARCHON begins execution by reading several input files. These files fall under the heading of INPUTS in Figure 2-1. The first file specifies the conditions the calculation is expected to maintain throughout the numerical integration. These conditions include the maximum error allowed to be propagated, specification of the time mesh for output, the minimum species concentration below which a species is not allowed to adversely impact the calculation, and where to find any driver data which the user had the option of using to externally drive a particular kinetic system.

These external driver inputs include $T_i(t)$, $T_e(t)$, $T_n(t)$, $\rho(t)$, and $q(t)$ contained in files, in tabular form, all as functions of time. Isothermal and isobaric kinetic problems are solved with ARCHON by omitting external driver files. A file defining the kinetic system is

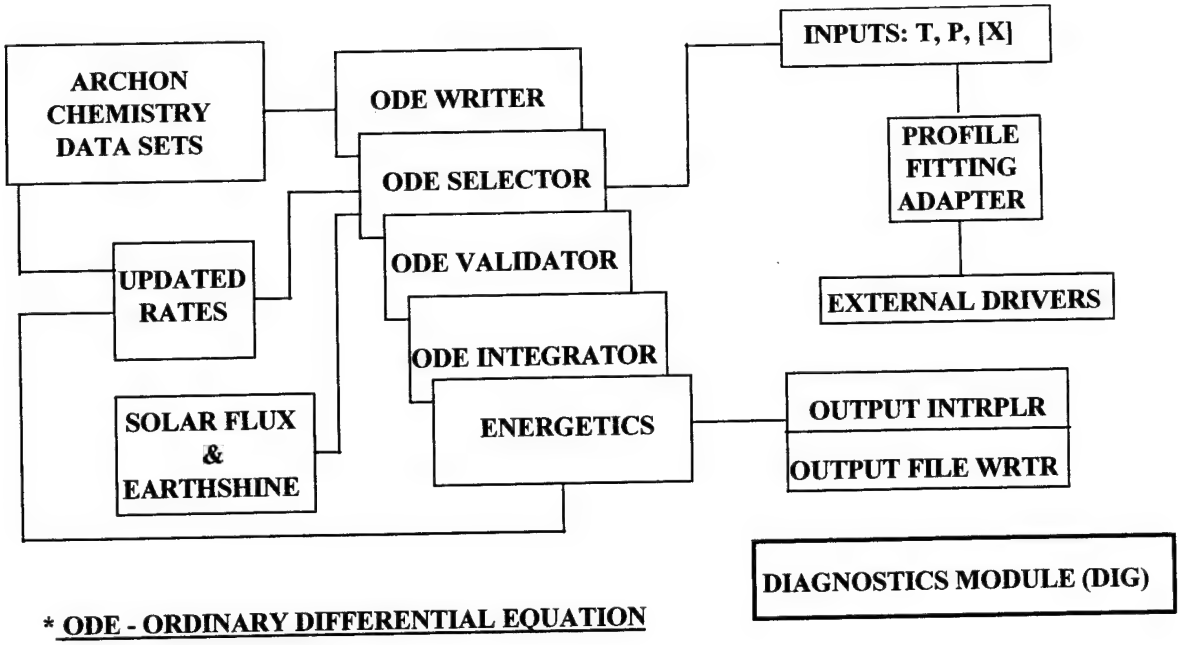

Figure 2-1. Schematic diagram of ARCHON code architecture

required by ARCHON. This file must contain the species names, their initial concentrations and, as an option, their enthalpy and chemical degeneracy.

ARCHON "reads in" the chemical kinetics data bases. These data bases fall under the functional block "ARCHON Chemistry Data Sets" in Figure 2-1. The user can substitute, with ease, a user-defined data base. ARCHON reads in each reaction from the data base and then uses the ODE WRITER function to assimilate each reaction from into the stoichiometry arrays which are retained and used throughout the calculation.

Once the reactions are read, ODE SELECTOR calls UPDATED RATES to calculate each reaction rate coefficient, and if necessary, calls SOLAR FLUX & EARTHSHINE, updating the radiation field. ODE SELECTOR neglects any reactions which are either undefined or negligibly important for the current temperature. As the temperature of the system evolves, either by external drivers or by internal thermodynamics, ODE SELECTOR continually tests all reactions automatically including or excluding each at each integration step relative to their changing importance.

ODE SELECTOR also excludes reactions whose reactants or products have not been specified by INPUTS, providing the user the freedom to experiment with subsets of larger problems. In conjunction with the DIG post-processor, the user has flexible capabilities to identify minimally acceptable data bases faithful to the overall chemistry of the kinetic system for system-oriented code operations.

Duplicated reactions, if any, are flagged by ODE SELECTOR prior to the start of the integration. ODE SELECTOR alerts the user of possible problems when duplicated

reactions are found in the data base. A file called REACTDUP is written containing a list of the duplicated reactions. It is up to the user to make informed judgments or obtain user support regarding the use of duplicate reactions. There are classes of reactions where identical reactions will contain rate data that are valid in different temperature ranges. These reactions will be flagged by ODE SELECTOR, but they will be properly handled as the temperature changes as previously outlined.

ODE VALIDATION constrains the numerical method within physical bounds throughout the numerical integration. If a species concentration becomes too small, ODE VALIDATION suspends its impact on the chemical system. In the absence of this restraint, the KINETX numerical method continues to track decaying species down to unrealistic concentrations, ultimately creating catastrophic numerical underflow conditions in many computer environments. ODE VALIDATION ensures that once a species has ceased contributing an observable to the system of interest its removal is performed conservatively, efficiently and correctly. If the removed species later emerges above the user-selected level that matters, ODE VALIDATION then includes it in the time-step tracking.

The ODE INTEGRATOR is the backbone of ARCHON. ODE INTEGRATOR is based on rigorously correct fundamental methods. Whereas Runge-Kutta, Adams, and other numerical methods approximate the time derivatives for each species, ODE INTEGRATOR calculates each derivative exactly. This was originally accomplished with the numerical solution expressed as a Taylor Series in time. The current ODE INTEGRATOR, the GEAR method, effectively accomplished the same result but in a more efficient manner. ODE INTEGRATOR determines the best time step to advance its numeric solution. It numerically integrates its solution, at the same time controlling unconstrained error propagation, ensuring that the numerical method in ARCHON is stable. The ODE INTEGRATOR performs another vital task during the calculation. A part of the ODE INTEGRATOR (KXNPSS) evaluates whether a particular species is stiff, and, if so, removes the mathematical manifestation of that stiff species from the calculation.

ENERGETICS provides the user with the option of monitoring the change in kinetic temperature caused by release or binding of chemical energies. A simple bookkeeping routine is used to determine the amount that the enthalpy of the system has changed from the prior step. The temperature changes of the neutral and ion species are then calculated. The electron temperature is altered on a phenomenological basis using the continuously slowing down approximation derived by Carron (see bibliography).

ARCHON continues to advance the solution, step by step, until the end of the desired time domain is reached. During the numerical integration, the solution periodically advances past-previously established grid points. As the solution advances past each grid point, the integrator is backward-interpolated to find and store the value of each species exactly at each grid point. When the calculation is complete the time/concentration history of each

species, time step versus time history, and temperature history is written to binary or ASCII files (user-selectable) for subsequent analysis.

Diagnostic post-processing support is provided by an ARCHON adjunct package called DIG. DIG is coded similarly to ARCHON, with the same overall design objectives. DIG will be discussed in another section and its operation is outlined in detail in the DIG User Guide.

2.2 ARD_5: REACTION RATE DATA SETS IN ARCHON.

The ARCHON code is unique in several aspects of its approach to first principles chemistry. Unlike many other codes, where at least parts of the actual chemistry involved are often imbedded in the executable code, ARCHON places the chemistry into separate data bases. The ARCHON data bases employ a non-constrained format, easily allowing users to create or modify complex problem descriptions. This format also allows for the maintenance of the data base as a reference document. Current rate data and its reference are easily added to the data base. Frequent updating and critical review assures users working with the ARCHON data bases that the rate data is the best available. The non-constrained format, along with retention of old rate data with its reference provides users an audit trail to track evolution of the current rate data.

ARCHON data bases are written in a free-formatted plain language form. Reactions are listed as they normally appear, with the addition of rate coefficient information following the reaction. An example of a typical entry in the ARCHON-D data base is listed below.

```
*****************************************************************
          0(1D)  +  H20(000)  <--->  OH  +  OH      2.20D-10
*
* Reviewed overall in DeMoore et al, "Chemical Kinetics and
* Photochemical Data for USe in Stratospheric Modeling",
* : JPL 85-37  (1985)
*
* Streit, G.E. et al, J. Chem. Phy., 65 4761 (1976)
*
* Davidson et al, J. Chem. Phys., 67, 5021 (1978)
*
*****************************************************************
```

The only requirement in entering a reaction to the data base is that the individual species' names are separated by a " + " and that the reactants and products are separated from one another with an arrow, "--->". Inclusion of a "double-headed" arrow invokes an internal calculation of the reverse rate by detailed balance. The ARCHON data base reader module (READRX) admits the inclusion of extra spaces in the definition of reactions. Extra spaces permits the user to make data base entries orderly and legibly. ARCHON checks every reaction before it is used to verify that the species which are included in the reaction are defined in the initial species listing.

ARCHON accomplishes its free-formatted style by examining each character and equating a character string to a specific species, and ignoring leading and trailing spaces. Each

species name or kinetic data entry need not fill particular fields for ARCHON to read the data base. Users who choose to construct data bases must ensure that each individual species' name remains consistent throughout the data bases ARCHON uses. Users who rely on the current DSWA Standard data base, ARD_5, must use the nomenclature for each species in this data base. Since thousands of reactions may be maintained in the data bases, it is possible that mixing equivalent names (i.e. $N_2(1)$ and $N_2(v=1)$) could be entered inadvertently in different sections of a data base causing exclusion of a large class of reactions.

To aid the user in identifying potential nomenclature problems, two files are written when the kinetic data base is initially read by ARCHON. The first file, called REACTUSE, lists all the reactions input from the data base. Those reactions whose data is correctly read are numbered, while those reactions that are not used are flagged with an asterisk next to the species name that ARCHON was unable to match. The offensive name is most often an undefined species (one that was defined differently or was omitted from the species list).

A second file, REACTDUP, contains a list of duplicated reactions. Each duplicated reaction is flagged in pairs by the reaction numbers referred to in REACTUSE. For example, if the 10^{th} reaction is a duplicate of the 2^{nd} reaction, e.g. the first and second reactant are swapped, REACTDUP will group the 10^{th} and 2^{nd} reaction together showing users that each reaction is identical. The user can then make the necessary corrections to the data base being used. While there are instances where duplicate reactions are needed (i.e. a reaction whose data differs in several different temperature ranges), it is easy to overlook a reaction previously listed when the order in which the reactants or products appear is different. The use of these two files, REACTUSE and REACTDUP, helps the user maintain data bases with the assurance that the reaction only appears once and that all reactions have defined initial conditions.

Following the reaction, on the same line, is the rate coefficient data. The general specification of a reaction has the form

$$R_1 + R_2 + R_3 \text{ ---> } P_1 + \ldots + P_8 \qquad A\ B\ C\ D\ E \qquad [T_1<T<T_2]\ |\text{USRSUB}$$

ARCHON offers three standard forms for the temperature dependence of the rate coefficient. The Arrhenius equation

$$k(T) = A * (T/300)^B * e^{(-1000 * C)/T^{(1/D)}} \tag{2.1}$$

is used when the given A coefficient is positive. Third body saturated reactions are handled using the formulation,

$$k(T)_{eff}=k(T)*M/(1+(k(T)*M)/k_{inf})*0.6^{(1+(\log(k(T)*M/kinf)))^{-1}} \tag{2.2}$$

and k_{inf}=E when E is specified along with A, B, C, and D. When A is negative, an

alternative power series is used,

$$k(T) = (-A + B * T^2 + C * T^3 + D * T^4) * e^{(-1000*E)/T^{(1/D)}} \quad (2.3)$$

Although most reactions can be represented by one of the above forms, there are some reactions not easily described by these standard formats. In such cases, a subroutine name is attached to the end of the reaction. A user-provided subroutine can then be written to describe the temperature dependence of the individual reaction.

Following the reaction portion of the entry is the reference information. The first reference listed is the source for the rate coefficient data used in the listing. Additional references contain information regarding the reaction but may not report the same rate coefficient being used in the data base. This provides the user with additional information which may be helpful maintaining the data base with the most current information, as well as providing sources for alternative rates.

Continuing activity is maintained on updating the DSWA/NWE data bases for use with the ARCHON (or other) code(s). To date, five data bases have been annotated and revised which include the air chemistry data base and a thermal vibraluminescence data base, which have now been combined in ARD_5. These data bases are continually circulated throughout the community for critical review. The form of the data bases is such that they are highly readable and can therefore be analyzed without difficulty. Since the chemistry is not embedded in code, it can be revised easily and the revisions noted for future reference. The data base contains many thousands of reactions involving many hundreds of species. This large volume of reaction data is maintained so that users may choose to employ the entire data base or subsets of the data base.

The addition of references directly into the text of the data base, along with the large number of reactions that are maintained, allows the ARCHON data bases to be used not only as input to the ARCHON code but also as a single standard reference for rate coefficient information. Every attempt has been made to make the databases as useful as reference resources as they are as input to the code.

Since the data bases can have thousands of reactions, locating any given reaction could pose a problem. In ARD_5, this large collection of reactions is broken down into sub-categories (similar to classifications used in the DNA handbook). Each sub-category is further organized using a simple set of rules (these rules can be found in the introduction to the data base). The organization of the data base into categories and sub-categories was implemented solely to assist users employing the data base as a reference, and is in no way necessary for use with the ARCHON code.

2.3 DIG: THE ARCHON DIAGNOSTIC POST-PROCESSOR.

When running large complex problems, analyzing the reaction set for completeness and efficiency is a difficult task. A diagnostic post processor has been developed to aid users

in evaluating the reaction database. DIG, the diagnostic module, uses number density profiles generated by the ARCHON code to determine the rates of reactions at a specific time. The use of this post-processing tool allows users to numerically diagnose the importance of particular reactions. Thus, reactions that are insignificant can be eliminated from the data set. Conversely, if a new reaction is being considered, investigating its contribution to the kinetic system can be assessed before it is actually added to the reaction set. The ability to diagnose potential additions to the databases is helpful when minimizing the chemistry for specialized applications, i.e. hydrodynamic calculations, without forsaking accuracy of the calculation.

When evaluating the reaction set, it is important to keep in mind that although the impact of a reaction on one species may be insignificant, it is possible that the reaction may contribute to the other species involved. It is therefore best to examine the impact on all species involved in a reaction. It is also important to verify the significance of a reaction over a time range, since a trivial reaction may become important at a later time. The need to examine reaction sets from several different points of view has required the diagnostics package to be versatile. To study the database as completely as possible the ARCHON diagnostics code has been written to operate in two different modes - preliminary screening or post-processing. Either mode may be selected from an initial menu, the output of which can be directed to the console or to a user specified file for later analysis.

"Preliminary Screening", sifts through the data base and finds those reactions controlling the production and destruction of a particular species from the reaction list. "Post-Processing" performs a similar function with the ARCHON output at given time steps. The user is required to input the time and the species of interest. The species may be entered either as a character string or by species number. To aid the user, a listing of the species set may be called up. The output is a table of those reactions involved in the production and destruction of the specified species. The rates of the reactions are calculated and the list sorted from the largest rate to the smallest. This screening is helpful in identifying both those reactions which are and are not important in the production or destruction of the species specified. The reaction information can then be used later to obtain more complete data on its importance.

SECTION 3
ARCHON USER MANUAL - GETTING STARTED

3.1 OVERVIEW.

Figure 3-1 is a graphical representation of the files necessary to run ARCHON, and the type of information generated by the code. To run a kinetics problem with ARCHON, three files are required; one containing a species list, one containing a reaction set, and the ARINIT file. The file containing the species list is used to define the species involved and their initial densities. The file containing the reaction set lists the reactions and rate coefficient data for the given kinetics problem. The last required file, called ARINIT, serves two purposes. Primarily, it is used as a road map providing ARCHON the names of the species list file, the reaction set file, and where to find them. Secondly, ARINIT initializes some basic operating parameters for ARCHON. In addition to these three required files, there are a number of optional files that may be used to constrain the problem by temperature, density, or ionization. ARINIT also informs ARCHON if any of the optional files are being used and where they are located. Using the three required files and any combination of the optional files, ARCHON can then solve the kinetics problem presented.

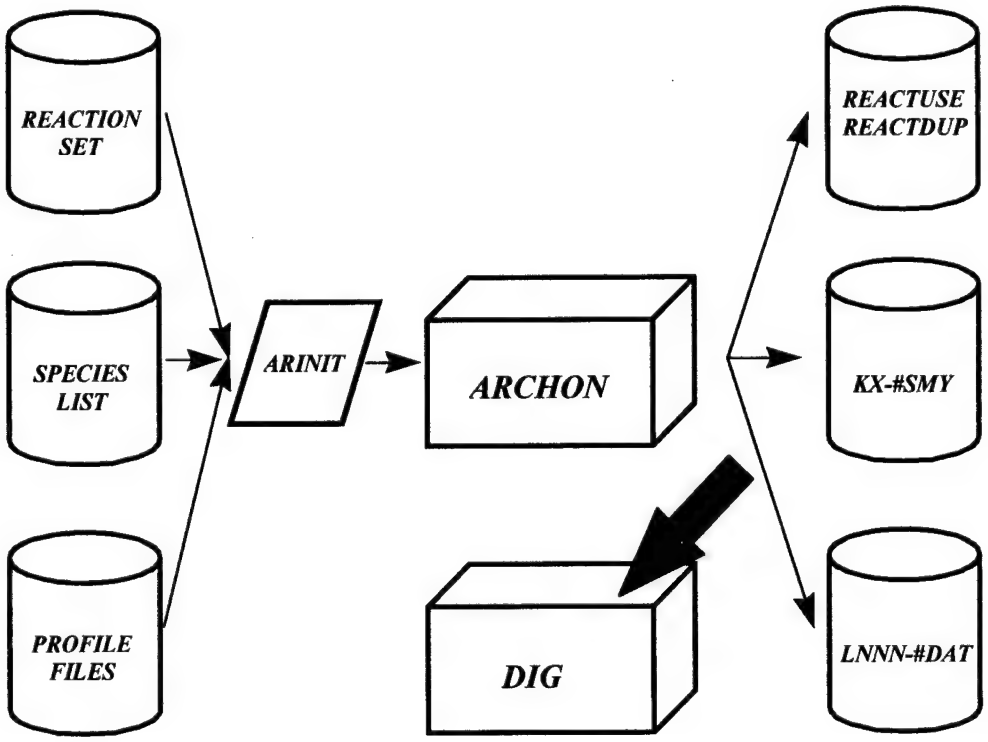

Figure 3-1. Graphical representation of the operating modules in ARCHON.

To illustrate the use of ARCHON, a sample problem is included with the software. In addition to ARCHON, the files supplied are, SPECIES, REACTSET (ARD_5), and ARINIT. The user may want to examine each of these files. With these files, the user can execute ARCHON by simply by typing "*ARCHON58*" on a PC or the appropriate machine dependent execution command.

As ARCHON begins the computation process, some of the input data is echoed to the screen. First, the species list is output, followed by the number of species and reactions that are actually going to be used. After reading the reaction set, ARCHON outputs a sequence marker to the screen during every step of the integration so that the user knows that the computation is proceeding.

Prior to integration, ARCHON writes to the screen the index number for the run. ARCHON can store solutions from up to 10 separate runs in the same directory. Each run is identified by an index number. This is followed by several lines of output describing the parameters of the problem. ARCHON then begins integrating the solution. As the solution advances, an optional line of output is directed to the screen. The values output correspond to the following variables:

time time step # of steps # of stiff species species controlling time step cpu time

After ARCHON completes the calculation, a summary of the final concentrations of all the species is displayed. This summary is also written to the KX-#.SMY file. The first time ARCHON is run, the index will be 0 and the corresponding summary file will be called KX-0.SMY.

Prior to the termination of ARCHON, several output files are generated. Some of these files are used for diagnostic purposes (REACTSET, REACTUSE, KX-#.DAT), and others contain the ARCHON solution to the problem (LNNN-#.DAT). The diagnostic files are in ASCII format and can be examined directly. The solution files are BINARY or ASCII formatted files which can be analyzed using any standard graphics routine. They represent species concentrations corresponding to the TIMES-#.DAT file.

The solution files may also be used with the diagnostic post processor, DIG, to perform a more detailed analysis of the reaction set. One feature of DIG allows users to determine the major reactions contributing to the production or removal of a species at a given time. A second feature of DIG allows users to determine how important a reaction is to the overall system for the time frame of the problem. Both capabilities allow users to decide which reactions are truly necessary for a given problem. A more complete description of DIG can be found later in this report.

3.2 REQUIRED INPUT FILES.

This section presents a sample problem to illustrate step by step the operation of ARCHON. This discussion includes a detailed look at each file and illustrates how to construct them.

There are three files which are required to solve a kinetics problem with ARCHON. These files can be constructed in any order, but all must be present in order to run ARCHON. The first file constructed here is the reaction set. The reaction set used can be any list of reactions. The file ARD_5.set provided with ARCHON, is a large set of air chemistry reactions that may be used in its entirety, or sub-sections may be extracted to be used independently. It should be understood that any set of reactions can be used. If the user wishes to compose a specific reaction set, there are only a few constraints to which the user must adhere. First, the species must be separated with a "+", and second, the reactants are separated from products with "--->". Field specifications do not exist, and therefore the set may be written in a free-format manner. The rate coefficient information for a given reaction is usually specified with the set of coefficients: A B C D and E. Depending on how these coefficients are represented, one of three standard equations will be used to calculate the rate. A more complete description of the database can be found in the previous section. An example of how a reaction is written is

```
N   +  O2     ---> NO   +  O        4.40E-12  0.00  3.22          (3.1)
```

Comments may be added to the reaction set by placing the symbol, "*", in column one. This symbol in column one may also be used to exclude a reaction from the calculation.

Table 3-1 shows an example reaction set. The name of this specific file is "REACTSET". This name is arbitrary and users may rename this file as long as this name (case sensitive) is specified in ARINIT. Notice that at the end of the file there is a "$". This is recognized by ARCHON as an end of file marker. It must be placed in the first column on the last line of the file to signal ARCHON at the end of the reaction set data.

After the reaction set is constructed, the next step is to create the species file. In this file, all species involved in the reaction set are defined and their initial concentrations are given. It is important to note that the nomenclature used in the species file should correspond *exactly* to the nomenclature used in the reaction set. Thus, in defining a species, if N is used in the reaction set to describe the ground state of nitrogen then in the species list N should also be used, not N(4S). *This point is very important: if a species is defined differently in the species list, reactions involving that species will not calculated.*

The first line of the file must be the title of the problem, and here we will write "EXAMPLE PROBLEM". The second line is the temperature used to calculate the rate coefficients. For this problem we will use "224.0" (K). An option to override this constant temperature with variable temperature profiles will be discussed later. The next input is the altitude. This value is used for some altitude-dependent reactions contained in ARD_5.set. We use 80 km in this example. The next input represents the day/night condition and is ".True." for day and ".False." for night. These are used for time-of-day-dependent rates. Following this information are the species definitions. As in the reaction

Table 3-1. ARCHON reaction set example.

```
-------------------------------------------------------------------------
N       +  O2          ---> NO      +  O          4.40E-12  0.00  3.22
N(2D)   +  O2          ---> NO      +  O          1.60E-12  0.50
N       +  NO          ---> N2      +  O          2.50E-11
N(2D)   +  NO          ---> N2      +  O          6.00E-11
N       +  NO2         ---> NO      +  NO         6.00E-12
O       +  NO2         ---> NO      +  O2         9.00E-12 -0.53
NO      +  O3          ---> NO2     +  O2         1.80E-12  0.00  1.37
N       +  O3          ---> NO      +  O2         1.00E-12  0.00  2.40
O       +  O    + M    ---> O2      +  M          4.32E-32 -1.50
N       +  N    + M    ---> N2      +  M          3.40E-32 -0.80
N       +  O    + M    ---> NO      +  M          1.00E-32 -0.50
O       +  O2   + M    ---> O3      +  M          6.00E-34 -2.30
O       +  NO   + M    ---> NO2     +  M          1.00E-31 -1.60
N       +  N           ---> N2                    1.00E-17 -0.90
O       +  NO          ---> NO2                   7.00E-18 -2.00
N       +  O           ---> NO                    2.00E-17 -0.35
N2+     +  e           ---> N(2D)   +  N          2.65E-07
N2+     +  e           ---> N(2D)   +  N(2D)      1.70E-07 -0.40
O2+     +  e           ---> O       +  O          2.00E-07 -0.70
NO+     +  e           ---> N       +  O          1.02E-07 -0.37
NO+     +  e           ---> N(2D)   +  O          4.00E-07 -0.90
O+      +  e    + e    ---> O       +  e          1.00E-19 -5.00
N+      +  e    + e    ---> N       +  e          1.00E-19 -5.00
O2(1D)  +  O3          ---> O2      +  O2   +  O  5.20E-11  0.00  2.84
O2(1D)  +  N           ---> O2      +  N          3.00E-15
O2(1D)  +  O           ---> O2      +  O          1.00E-16
O2(1D)  +  e           ---> O2      +  e          2.31E-12  1.50
O2(1D)  +  N2          ---> O2      +  N2         1.40E-19
O2(1D)  +  O2          ---> O2      +  O2         1.70E-18  0.80
O2(1D)                 ---> O2      +  hnu(1.27)  2.60E-04
O       +  O3          ---> O2(1D)  +  O2         8.00E-12  0.00  2.06
O       +  O3          ---> O2      +  O2         8.00E-12  0.00  2.06
N2+     +  NO          ---> NO+     +  N2         3.30E-10
N2+     +  O2          ---> O2+     +  N2         5.00E-11 -0.80
N2+     +  O           ---> O+      +  N2         1.00E-11 -0.23
N2+     +  N           ---> N+      +  N2         1.00E-11
N+      +  NO          ---> N       +  NO+        3.00E-10 -0.27
N+      +  O2          ---> N       +  O2+        1.50E-10
N+      +  O           ---> N       +  O+         2.00E-12
O+      +  NO          ---> NO+     +  O          1.30E-12
O+      +  O2          ---> O2+     +  O          2.00E-11 -0.50
O2+     +  NO          ---> NO+     +  O2         6.30E-10
O2+     +  N2          ---> NO+     +  NO         1.00E-16
N+      +  O2          ---> O       +  NO+        1.80E-10
N+      +  O2          ---> NO      +  O+         4.00E-11
O+      +  NO          ---> O2+     +  N          1.00E-13
O+      +  N2          ---> NO+     +  N          1.20E-12 -1.00
N2+     +  O           ---> NO+     +  N(2D)      1.30E-10 -0.46
N2+     +  O           ---> NO+     +  N          1.45E-11 -0.46
O2+     +  NO2         ---> NO+     +  O3         1.00E-11
O2+     +  N           ---> NO+     +  O          1.20E-10
O2      +  e    + O2   ---> O2-     +  O2         1.40E-29 -1.00  0.60
O2-     +  O2          ---> O2      +  O2   +  e  2.70E-10  0.50  5.59
O2-     +  N2          ---> O2      +  N2   +  e  1.90E-12  1.50  4.99
O2(1D)  +  O2-         ---> O2      +  O2   +  e  2.00E-10
O2      +  e    + N2   ---> O2-     +  N2         1.00E-31
O2-     +  O           ---> O3      +  e          1.50E-10
O2-     +  N           ---> NO2     +  e          3.00E-10
$
-------------------------------------------------------------------------
```

set, a free-format style can be used since field specifications are not defined. For each species involved, the following information should appear on a single line:

species name initial density enthalpy degeneracy

The species name should reflect the name used in the reaction set. Table 3-2 is an example of a species list. For certain problems, some of the species' concentrations are not expected to change or are held at a fixed value as part of the problem definition. These densities must be at the end of the species list file and must be preceded by a line with an "&" in column 1. As in the reaction set file, a "$" in column 1 designates the end-of-file.

Table 3-2. ARCHON species list example.

```
Example Problem
224.0
80.
.TRUE.
e           2.2d+12        0.0000     2.0
O2          1.6d+14        0.0000     3.0
O2(1D)      8.0d+11        0.9970     5.0
N2          6.2d+14        0.0000     1.0
NO          1.1d+06        0.9950     6.0
NO2         5.0d+04        1.1570     1.0
O3          1.5d+08       -0.6000     1.0
N2+         1.5d+12       15.5800     2.0
N+          3.0d+11       10.4200     3.0
O2+         3.0d+11       12.0630     2.0
O+          1.0d+11       16.1750     4.0
N           1.4d+12        4.8800     4.0
N(2D)       9.2d+11        7.2640    10.0
O           2.8d+12        2.5800     3.0
hnu(1.27)    0.000         0.9970     1.0
NO+          0.000        10.1980     1.0
O2-          0.000        -0.4290     4.0
&
M           7.86d+14        0.0000     1.0
$
```

With the reaction set and the species list now constructed there remains only one other required file, ARINIT to be created. Unlike the other two files, this file must be called **ARINIT**. ARINIT is a road map for ARCHON and it shows ARCHON where to find the reaction set file, the species list file and optional profile information. A second task for ARINIT is to set up some of the initial parameters used in ARCHON. A template for ARINIT looks like

```
spin
rxin
tefl
tifl
tnfl
```

```
dnfl
qfl
ordr
erps
lnlg
tmin
tmax
ymin
oflg
mflg
```

This template serves only to assist the user in constructing an appropriate file. Values for the variables must appear after column 5 in order to be read correctly by ARCHON. ARCHON does not provide default values, therefore the user must complete the entire file. The species file name should appear after *spin* followed by the reaction set name on the second line after *rxin*. If the file exists in a different directory, the path may be added to this name. The path and the file name cannot exceed 80 characters. Extensions are used only as they apply to the name of the file. The next five lines of the file refer to the names of optional profile files. These are files that allow users to constrain the problem. A more lengthy discussion of these files appears later in this section. Since these files are optional their names are also specific to their use. If a user wishes not to exercise the optional files, "none" or "NONE" must be written after the variable name. The first 7 lines of the ARINIT file should look something like

```
spin    SPECIES
rxin    REACTIONS
tefl    none
tifl    none
tnfl    none
dnfl    none
qfl     none
```

In this example, the temperature profiles (tefl, tlfl and tnfl), the density constraining file, dnfl, and the ionization file, qfl, are not used. This is the end of the road map section of ARINIT. The rest of this file sets the controlling parameters for the execution of ARCHON.

The controlling parameters set up various constrains on how ARCHON will execute the problem. The first parameter, ordr, sets the order of the Taylor Series integration method, if that option is chosen. The next parameter, erps, limits the amount of error that will be allowed to propagate from step to step. Typically a value of 1.0E-05 is used. The third setup parameter signals ARCHON whether to output files on a linear grid (1) or a logarithmic grid (2). A "-" sign in front of the number specifies ASCII file output. Lack of a sign specifies binary file output.

The next two parameters, tmin and tmax, define the time domain over which the solution will be displayed. The parameter ymin is the minimum species concentration below which ARCHON will ignore the value in calculating the time step as the solution advances. If oflg is 'y' ARCHON writes information to the screen at the end of every time step. If ARCHON is run in a batch mode, this feature should be deactivated by using an 'n'. The last parameter in ARINIT is mflg. This variable tells ARCHON what type of numerical

integration method will be used. For almost every case, a value of "2" should be used, which specifies the modified GEAR integration method. A value of "1" results in an integration using the Taylor series method with the NPSS transformation. A value of "0" specifies that ARCHON will use the Taylor series method without the NPSS transformation. This method is very time consuming and should only be used to test the integrator. An example of a complete ARINIT file is shown in Table 3-3.

Table 3-3. Example of the ARINIT file.

```
-----------------------------------------
                spin    SPECIES
                rxin    REACTIONS
                tefl    none
                tifl    none
                tnfl    none
                dnfl    none
                qfl     none
                ordr    5
                erps    1.0E-05
                lnlg    -1
                tmin    1.0E-05
                tmax    8.0E+01
                ymin    1.0
                oflg    y
                mflg    2
-----------------------------------------
```

3.3 OPTIONAL INPUT FILES.

ARCHON is a flexible tool that can solve many different types of kinetics problems. External Drivers are provided giving users the option of constraining the system in any one of five different ways. ARCHON uses these External Drivers by applying data from profile files. These files allow the user to impose a set of conditions that define the temperature (electron, ion, and neutral), density and ionizing energy deposition rate (eV cm^{-3} s^{-1}) for the kinetic system over the period of integration. When using the temperature profile files, it is necessary to specify all three temperatures; electron, ion and neutral. These files are all set up very similarly. The same temperature profile may be used for all three or entirely different temperature profiles may be used. There should be a time and a constraining value for each line of the file. Examples of an electron temperature profile, an ionizing energy deposition rate profile and a density driver profile are given in Table 3-4.

ARCHON uses the values supplied by the External Drivers to interpolate between the values so that the system can be constrained throughout the integration. Care should be taken to include enough points in the file so that the interpolation routine can accurately define the feature of the constraining set. *An error will result if the time domain of the External Driver does not match the time domain set in the ARINIT file.*

Table 3-4. An electron temperature profile, an ionizing energy deposition rate profile and a density driver profile. Note that the density is a fractional multiplier coefficient.

Time(s)	Temp. (K)	Time (s)	EDEP (eV cm^{-3} s^{-1})	Time (s)	Density
1.0000E-05	1044	1.0000E-05	4.999E+09	1.0000E-05	1.000
1.0000E-03	1044	1.0000E-03	4.994E+09	1.0000E-03	1.000
1.0000E-02	1044	1.0000E-02	4.940E+09	1.0000E-02	1.000
1.0000E-01	1044	1.0000E-01	4.459E+09	1.0000E-01	1.000
1.5000E-01	1044	1.5000E-01	4.228E+09	1.5000E-01	1.000
1.5020E-01	1075	1.5020E-01	4.227E+09	1.5020E-01	1.000
1.5030E-01	1090	1.5030E-01	4.226E+09	1.5030E-01	1.000
2.0000E-01	1110	2.0000E-01	4.017E+09	2.0000E-01	1.000
3.0000E-01	1130	3.0000E-01	3.649E+09	3.0000E-01	1.000
4.0000E-01	1150	4.0000E-01	3.339E+09	4.0000E-01	1.000
5.0000E-01	1160	5.0000E-01	3.073E+09	5.0000E-01	1.000
7.5000E-01	1160	7.5000E-01	2.554E+09	7.5000E-01	1.000
1.0000E+00	1160	1.0000E+00	2.176E+09	1.0000E+00	1.002
1.5000E+00	1270	1.5000E+00	1.665E+09	1.5000E+00	1.004
2.0000E+00	1393	2.0000E+00	1.337E+09	2.0000E+00	1.008
3.0000E+00	1625	3.0000E+00	9.473E+08	3.0000E+00	1.012
4.0000E+00	1800	4.0000E+00	7.247E+08	4.0000E+00	1.000
5.0000E+00	2000	5.0000E+00	5.823E+08	5.0000E+00	0.981
6.0000E+00	2100	6.0000E+00	4.840E+08	6.0000E+00	0.900
7.0000E+00	2200	7.0000E+00	4.123E+08	7.0000E+00	0.800
8.0000E+00	2300	8.0000E+00	3.580E+08	8.0000E+00	0.700
9.0000E+00	2400	9.0000E+00	3.154E+08	9.0000E+00	0.600
1.0000E+01	2450	1.0000E+01	2.813E+08	1.0000E+01	0.576
2.0000E+01	1900	2.0000E+01	1.295E+08	2.0000E+01	0.600
3.0000E+01	1400	3.0000E+01	8.115E+07	3.0000E+01	0.700
4.0000E+01	800	4.0000E+01	5.802E+07	4.0000E+01	0.800
4.2000E+01	700	4.2000E+01	5.480E+07	4.2000E+01	0.820
4.4000E+01	600	4.4000E+01	5.189E+07	4.4000E+01	0.840
4.6000E+01	500	4.6000E+01	4.925E+07	4.6000E+01	0.860
4.8000E+01	400	4.8000E+01	4.685E+07	4.8000E+01	0.880
5.0000E+01	350	5.0000E+01	4.465E+07	5.0000E+01	0.900
5.2000E+01	350	5.2000E+01	4.264E+07	5.2000E+01	0.905
5.4000E+01	350	5.4000E+01	4.078E+07	5.4000E+01	0.910
5.6000E+01	350	5.6000E+01	3.907E+07	5.6000E+01	0.915
5.8000E+01	350	5.8000E+01	3.749E+07	5.8000E+01	0.920
6.0000E+01	350	6.0000E+01	3.602E+07	6.0000E+01	0.922
7.0000E+01	350	7.0000E+01	3.500E+07	7.0000E+01	0.988
8.0000E+01	350	8.0000E+01	3.500E+07	8.0000E+01	0.999

When a profile name is given in the ARINIT file, that option is used by ARCHON. Thus if a temperature is defined in the species list and a temperature profile file is used, it is the values in the profile files that are actually used in the calculation.

3.4 ARCHON-GENERATED OUTPUT.

ARCHON generates two different types of output: diagnostic and time history. Diagnostic output includes the files REACTUSE, REACTDUP and KX-#.smy which are helpful when setting up and debugging a problem. The diagnostic output files contain information about the reaction set and the rate coefficients calculated. REACTUSE

contains all the reactions that were used in the calculation. This file also marks those reactions which are not used. This is a particularly useful file for debugging. When a species is not defined in the species list, all those reactions that involve that species are not used. If a reaction is not listed in REACTUSE it may also indicate an error in the species file. A sample section of the REACTUSE file is given below:

```
1  N       +  O2        --->  NO     +  O        4.40E-12  0.00  3.22
2  N(2D)   +  O2        --->  NO     +  O        1.60E-12  0.50
  *N(4S)   +  NO        --->  N2     +  O        2.50E-11
3  N(2D)   +  NO        --->  N2     +  O        6.00E-11
```

Those reactions which are numbered are included in the calculation. Reactions that are not used are left unnumbered, and any species not in the species file is marked with an "*". In this example, the reaction that is not numbered was not included because N(4S) was not defined in the species list.

REACTDUP is another diagnostic file which helps to identify any duplicate reactions. When running an ARCHON problem for the first time, it is advisable to examine REACTDUP. Duplicate reactions are often difficult to detect when one is looking at a reaction set with several hundred reactions. In the REACTDUP file, the first reaction is used in the ARCHON calculation. The second is listed but not used. This is important in verifying the particular reactions desired in the calculation. One last thing to note about duplicate reactions: if a reaction is written twice with different temperature ranges, they will appear in this list even though only one reaction at a time is used.

The last diagnostic tool is the summary file KX-#.SMY. This file lists the reactions used in the problem, the calculated rate coefficients for the first time step, the initial species densities, the initial conditions of the problem, and the final species densities at the end of the calculation. An example of the last two parts of the KX-#.SMY is given in Table 3-5. The first block of data contains the initial condition of the problem, including the species concentrations at time zero. Following the first block are the results of the calculation at the end of the integration. The first column in this block is the species name. The species name is then followed by the final concentration. The third and fourth columns of numbers deal with the number of times that the species controlled the time step and how many times the species was determined to be stiff. The fifth and sixth columns are the first and second derivatives of the rate. Finally, the last column which contains either 'F' or 'T' tells the user if the species is below the threshold level set in ARINIT.

The second type of output generated by ARCHON is the time history of the solution to the kinetic system. For each species defined in the species list, an ASCII or binary file, Lnnn-#.dat is written that contains the densities of the species corresponding to the time step history file (TIMES-#.dat). In addition to the files for each species, there are the corresponding ASCII or binary output files for the temperatures used (Te, Ti, Tn) . These files can be used with any graphics package to display the time dependent nature of the species. An example of the type of plot generated with AXUM is given in Figure 3-2.

Table 3-5. A sample portion of the summary file KX-0.SMY.

```
Benchmark Example
-------------------------------------------------------------------------------
              eps = 1.0D-03  LinLog = 2  Tmax = 8.0D+01     mf=1
-------------------------------------------------------------------------------
      t=1.00d-05     h=0.0d+00          0 steps                    m =  5
-------------------------------------------------------------------------------
  1 [e                ]: 2.2000000D+12      0       0    0.0D+00   0.0D+00 F
  2 [O2               ]: 1.6000000D+14      0       0    0.0D+00   0.0D+00 F
  3 [O2(1D)           ]: 8.0000000D+11      0       0    0.0D+00   0.0D+00 F
  4 [N2               ]: 6.2000000D+14      0       0    0.0D+00   0.0D+00 F
  5 [NO               ]: 1.1000000D+06      0       0    0.0D+00   0.0D+00 F
  6 [NO2              ]: 5.0000000D+04      0       0    0.0D+00   0.0D+00 F
  7 [O3               ]: 1.5000000D+08      0       0    0.0D+00   0.0D+00 F
  8 [N2+              ]: 1.5000000D+12      0       0    0.0D+00   0.0D+00 F
  9 [N+               ]: 3.0000000D+11      0       0    0.0D+00   0.0D+00 F
 10 [O2+              ]: 3.0000000D+11      0       0    0.0D+00   0.0D+00 F
 11 [O+               ]: 1.0000000D+11      0       0    0.0D+00   0.0D+00 F
 12 [N                ]: 1.4000000D+12      0       0    0.0D+00   0.0D+00 F
 13 [N(2D)            ]: 9.2000000D+11      0       0    0.0D+00   0.0D+00 F
 14 [O(3P)            ]: 2.8000000D+12      0       0    0.0D+00   0.0D+00 F
 15 [NO+              ]: 5.0000000D-04      0       0    0.0D+00   0.0D+00 F
 16 [O2-              ]: 5.0000000D-04      0       0    0.0D+00   0.0D+00 F
-------------------------------------------------------------------------------
                              ARCHON Integ. Time:      :00
-------------------------------------------------------------------------------
      t=8.00d+01     h=9.3d-01       1344 steps   N             m =  5
-------------------------------------------------------------------------------
  1 [e                ]: 3.0242357D+04      0       0  -3.8D+02   4.7D+00 F
  2 [O2               ]: 1.5708178D+14      0       0   1.1D+09  -9.2D+05 F
  3 [O2(1D)           ]: 6.9869509D+11      0       0  -1.1D+09   9.2D+05 F
  4 [N2               ]: 6.2280690D+14      0       0   4.6D+01  -7.8D-01 F
  5 [NO               ]: 6.1953853D+09      1       0   2.9D+02  -3.7D+00 F
  6 [NO2              ]: 3.3252874D+03      1    -261   1.9D-05   2.8D-06 F
  7 [O3               ]: 2.4590076D+03     65       0  -3.3D+01   1.1D+00 F
  8 [N2+              ]: 5.4613501D-01     32       0   0.0D+00   0.0D+00 T
  9 [N+               ]: 7.8832331D-01     37       0   0.0D+00   0.0D+00 T
 10 [O2+              ]: 1.0775884D-08     26       0   0.0D+00   0.0D+00 F
 11 [O+               ]: 1.1828819D-10     30       0   0.0D+00   0.0D+00 F
 12 [N                ]: 2.9671782D+02    196       0  -1.0D+01   5.5D-01 F
 13 [N(2D)            ]: 1.0210666D+00    729    -262  -2.5D-02   4.8D-04 F
 14 [O(3P)            ]: 9.5333101D+12      0       0  -5.0D+05   1.3D+01 F
 15 [NO+              ]: 3.0242303D+04      4       0  -3.8D+02   4.7D+00 F
 16 [O2-              ]: 1.2816632D+00    223    -991  -1.6D-02   2.0D-04 F
-------------------------------------------------------------------------------
```

The unformatted files can also be used with the post-processor, DIG, to determine the completeness of their reaction set. Step by step instruction on the use of DIG is detailed later.

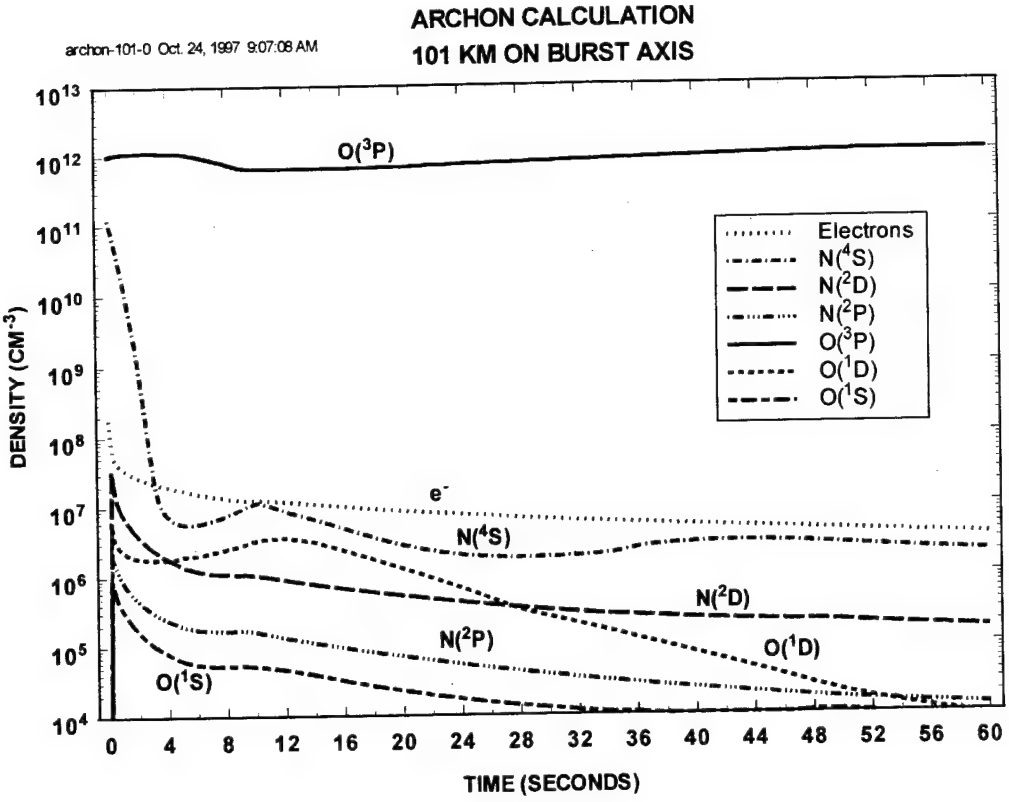

Figure 3-2. Example species density time-history plot generated by ARCHON.

SECTION 4
ARCHON58 USER'S GUIDE

4.1 ARCHON INITIALIZATION/START-UP FILE.

Required/Optional

Required File Name : arinit

Function : Used to input operating parameters.

Format :

spin *filename*
rxin *filename*
tefl *filename*
tifl *filename*
tnfl *filename*
dnfl *filename*
qfl *filename*
ordr *integer*
erps *real*
lnlg *integer (preceded by "minus" sign yields ASCII output - otherwise binary)*
tmin *real*
tmax *real*
ymin *real*
oflg *y or n*
mflg *integer*

Note that the variable inputs must start in column 6.

spin: Pathname to the Species Initial Density file.

rxin: Pathname to the Reaction Set file.

tefl: Pathname to Electron Temperature Profile file. Type none if a profile is not used

tifl: Pathname to Ion Temperature Profile. Type none if a profile is not used

tnfl: Pathname to Neutral Temperature Profile. Type none if a profile is not used

dnfl: Pathname to Density Profile. Type none
if a profile is not used

qfl: Pathname to Ionization Profile. Type none
if a profile is not used

ordr: Order of the Taylor Series Expansion. Typically, ordr is 5.

erps: Error-per-step criterion, usually set to 1.0E-05.

lnlg: Indicates whether the output time mesh is linear or log.
LnLg=1 for linear, LnLg=2 for logarithmic time grid.
Note that incerting a "minus" sign prior to the number results in ASCII output.
Omission of any sign results in BINARY output.

Tmin: The initial (i.e. minimum) value of time on the output grid.

Tmax: The final (i.e. maximum) value of time on the output grid.

Ymin: The minimum species concentration which will be allowed to
control the integration time step. Typically 1.0.

Oflg: A switch used to set ARCHON in an interactive mode or batch mode
"y" specifies screen interactive, "n" specifies no interaction (for batch)

Mflg: Indicates the type of integrator to be used.

0 Uses the Taylor series expansion without the stiffness correction. This should only be used in rare cases to check the integrator since it is very time consuming

1 Uses the Taylor series expansion with the stiffness corrector.

2 Uses the modified GEAR method - preferred for all calculations where the user is not "expert" at manipulation of integration techniques

4.2 ARCHON INITIAL SPECIES DENSITY FILE.

Required/Optional

Required File Name : Any name up to eight characters.

Function : Used to input the initial species concentrations.

Format :

```
Title
Temperature
Altitude
Day or Night
Species Name    Density    Enthalpy    Degeneracy
&
Species Name    Density    Enthalpy    Degeneracy
$
```

Title : May be any string up to 80 characters in length.

Temperature : This temperature is used when an external temperature profile is not given. Specification of a negative temperature will invoke Subroutine Energy, although the absolute value for the given temperature parameter will be used as the initial temperature.

Altitude : Altitude of the cell for which the calculation is done.

Day or Night : An input flag - T for day or F for night.

Species Name : All species appearing in the reaction list must be defined here. They should be named in this file exactly as they are in the reaction set.

Initial Densities : Initial concentrations, normally in units of molecules cm^{-3}. If a species does not have an initial concentration but is included in the reaction set, it should be listed and the density set to 0.0 .

Enthalpies + Degeneracies : These values are used in the detailed balancing of the reverse reaction when applicable. If no forward and reverse reactions are used these values may be listed as 1.0's.

& : This symbol separates the changing species from those species that remain constant throughout the calculation. The constant species should be input in the same manner as changing species.

$: This symbol denotes the end of the species file. IT MUST BE INCLUDED AT THE END OF THE LIST.

Note: A species can be eliminated from the set by using an asterisk (*) in column 1.

!!! WARNING !!!

Care should be taken when "commenting out" or eliminating species from the species list. If a species does not appear in this list, then all reactions involving that species will be ignored. Thus, an inadvertent elimination of a species will result in a calculation being done with an incomplete and/or inappropriate reaction set.

4.3 ARCHON REACTION SET FILE.

Required/Optional

Required Name : Any name up to eight characters.

Function : Used to input a reaction list and the corresponding rate coefficient information.

Format:

x + y ---> z + w A B C D E

If the user desires ARCHON to calculate both the forward and reverse reactions, the input is designated by a <--->. NOTE: This option should be used only where the number of reactants and products is the same to avoid problems in the detailed balance equation.

Species : All species used must be defined in the Initial Species Density List. Care must be exercised to use consistent nomenclature. A "+" must separate each species. When designating a positively charged species, no spaces should separate the name and the "+".

Rate Coefficient Information : The rate information should conform to one of the three following formats. If a rate will not fit into one of these formats a special subroutine can be written and called to calculate the rate. If A is positive, A, B, C, D, and E will use the following form for the temperature-dependent rate coefficient:

$$k(T) = A * (T/300) ** B * EXP(-1000 * C / T ** 1/D) \quad (4.1)$$

If E is specified, it is $k_{infinity}$, and k(T) is modified to account for third body saturation:

$$k(T)_{eff}=k(T)*M / (1 + k(T)\ M / kinf) * 0.6 ** (1 + (log10(k(T) *M/kinf) ** 2) **(-1) \quad (4.2)$$

If A is negative then an alternate power series will be used instead:

$$k(T) = (-A + B * T**2 + C * T**3 + D * T**4) * EXP(-1000 * E/T) \quad (4.3)$$

Note: Rate coefficient information should be input as real numbers.

Note: Reactions may be commented out by using a "*" in column 1, and comments may be freely interspersed throughout the reaction set.

4.4 ARCHON DENSITY PROFILE FILE.

Required/Optional

Required Name : Any name up to eight characters.

Function : Used to input an externally driven density profile.

Format :

Time Density

Time : The time is input in units of seconds.

Density : The density can be input in any consistent units. Note that the density designation is normally a fractional coefficient that multiplies the initial density by the fractional change in the density.

Note: The interpolation routine is a linear fit between adjacent points. Care should be taken to provide an adequate number of points to fully describe the function of the density. Up to 200 points may be used.

4.5 ARCHON TEMPERATURE PROFILE FILES.

Required/Optional

Required Name : Any name up to eight characters.

Function : Used to input externally driven temperature profiles.

Format :

Time Temperature (K)

Time : The time is input in units of seconds.

Temperature : The temperature should be input in units of degrees K.

Note: If a temperature profile is excluded, the isothermal default temperature from the initial species list will be used. The interpolation routine is a linear fit between adjacent points. Care should be taken to provide an adequate number of points to fully describe the function of the temperature. Up to 200 points may be used.

4.6 ARCHON IONIZING ENERGY DEPOSITION PROFILE FILES.

Required/Optional

Required Name : Any name up to eight characters.

Function : Used to input externally-driven ionization profile.

Format :

Time Energy Deposition Rate (eV cm^{-3} s^{-1})

Time : The time is input in units of seconds.

Energy Deposition Rate : The energy deposition rate *must be* in units eV cm^{-3} s^{-1}.

Note: The interpolation routine is a linear fit between adjacent points. Care should be taken to provide an adequate number of points to fully describe the function of the ionization. Up to 200 points may be used.

4.7 OUTPUT FILES GENERATED BY ARCHON.

REACTDUP : An ASCII file describing those reactions which are listed more than once in the reaction set.

REACTUSE : An ASCII file describing the reaction set. Those reactions that are used in the calculation are numbered while those not used, due to lack of sufficient input data for one or more species, are marked with a "*" next to the undefined species.

TIMES-#.DAT : An ASCII file describing the output time grid.

KX-#.SMY : A summary file which contains the reactions used, the calculated rate coefficients for the first time step, initial species concentrations, and the final species concentration at the end of the calculation.

Lnnn-#.DAT : Binary or ASCII files containing the concentration information for the individual species over the time grid. These files are used for plotting. "nnn" is the index number of the species.

TEME-#.DAT, TEMN-#.DAT, TEMI-#.DAT : Binary or ASCII files containing the temperature information corresponding to the time grid.

The -# indicates the index of the ARCHON run. Each time ARCHON is run in the same directory the results are stored in files with an index number. The index numbers will go from 0-9, thus enabling one to store the results from 10 ARCHON runs.

4.8 EXAMPLES OF ARCHON FILES

ARCHON INITIALIZATION/START-UP FILE: File Name = ARINIT *(required name)*

```
spin cesiumsh
rxin reactset.cs
tefl none
tifl none
tnfl none
dnfl none
qfl  none
ordr 5
erps 1.d-3
lnlg 1
tmin 0.0
tmax 1.
ymin 1.d-25
oflg y
mflg 1
```

ARCHON INITIAL SPECIES DENSITY FILE: File Name = CESIUMSH *(user name)*

```
 CESIUM  -  A Model of Induced Atmospheric Ionization
  300.0
  70.
  F
  e      1.00E2  0. 0.
  O2-    5.20D2  0. 0.
  Cs+    6.20D2  0. 0.
  Cs     1.00D12 0. 0.
  CsO2   0.00    0. 0.
  O2     3.60D14 0. 0.
&
  N2     1.00    0. 0.
  Hnu    1.00    0. 0.
$
```

ARCHON REACTION SET FILE: File Name = REACTSET.CS *(user name)*

```
* This is the cesium reaction set
 O2- + Hnu        ---> O2 + e              4.00D-01
 Cs+ + e  + N2    ---> Cs + Hnu + N2       1.00D-12
 O2- + Cs+        ---> Cs + O2             5.00D-08
 Cs  + Hnu        ---> Cs+ + e             3.24D-03
 O2  + Cs + Cs    ---> CsO2 + Cs           1.00D-31
 O2  + Cs + CsO2  ---> CsO2 + CsO2         1.00D-31
 O2  + Cs + N2    ---> CsO2 + N2           1.40D-16
 O2  + Cs + O2    ---> CsO2 + O2           1.00D-31
 O2  + e  + O2    ---> O2- + O2            1.24D-30
 O2  + e  + N2    ---> O2- + N2            1.40d-16
$
```

4.9 DIG USER GUIDE.

Function :

DIG, the ARCHON Diagnostic Module, is a user-interactive module designed to assist in the analysis of the data bases used in conjunction with ARCHON. DIG can operate in two modes, either as a data base analyzer or an ARCHON post-processor.

As an analyzer, it can be used to examine the data in the reaction data base. DIG will display all the reactions involved in the production or destruction of a given species with the calculated rate coefficients that will be used by ARCHON. The reactions are ordered based on the calculated rate coefficients.

As a post-processor DIG employs the files generated by ARCHON to examine the rates associated with reactions at a particular time in the ARCHON calculation. In this mode the concentration and temperature information is taken from the data output by ARCHON. Thus the rate calculated is consistent with the rate used in ARCHON at the prescribed time. The reactions are sorted by their rates and up to 20 reactions for each time step, in decreasing order of the rate, is listed. As a post-processor, DIG is a useful tool to assist a user in assessing the completeness of a chemistry data base in a particular calculation.

Required Files:

ARINIT	This file defines the name and location of the species list and reaction set files.
Species List	Names of species employed in a problem.
Reaction Set	The data base of reactions employed.

Optional Files:
(Required in post-processing mode.)

Lnnn-#.DAT	These are the ARCHON-generated binary or ASCII files which define computed number density vs time profiles.
TIMES-#.DAT	This is the time grid associated with the Lnnn-#.DAT file.
TEME-#.DAT TEMN-#.DAT TEMI-#.DAT	These are the temperature files generated by ARCHON.

Required Input:

Type of analysis ? Since DIG has the flexibility to operate as a pre-processor, to examine databases, and as a post processor to examine ARCHON generated results, it is necessary to specify the type of analysis that is to be done. The choices are
1= Data base analysis
2= Post-processing analysis

Index no ? This input is required when operating in a post processing mode. The prompt refers to the # of the Lnnn-#.DAT files.

Enter option no.?
1 = Preliminary Screening. Allows the user to analyze the reaction data base
2 = Impact Study. Allows the user to examine the impact of a specified reaction on the production and destruction of all the species involved in the reaction. ***(Note: This option is not operational at this time)***
3 = Output Options. Allows the user to direct the flow of the output to the console or a user specified file.
0 = Exit

Preliminary Screening:

Enter species name? The species may be input manually or chosen from a given list. If the species of interest is typed in, care should be taken to insure that the name is exactly as it appears in the species list. A list of species can be requested by typing a "0" when prompted for the species name. Associated with each species is a number. After the list has been requested, the user must refer to the species by its number.

Enter Time ? This input is required when operating in a post processing mode. The time must be between t=0 and the maximum time for which the ARCHON calculation was performed. Time is in seconds.

Output:

Title
Temperature
Altitude
Species Name Concentration Time
Production Reactions
 # a + b ---> c + d rate
Destruction Reaction
 # a + b ---> c + d rate

Title : Taken from the species list.

Temperature: Taken either from the species list in the preprocessor mode or from the temperature files (TEME-#.DAT, TEMN-#.DAT, TEMI-#.DAT) in the post processor mode. In both cases, the temperature listed is the value used in calculating the rate coefficient.

Altitude: Taken from the species list. The value list is what has been used to calculate altitude dependent rate coefficients.

Species Name: The name indicated.

Concentration:	The species concentration at the time indicted. Not displayed when pre-processing.
Time:	The time indicated. Not displayed when pre-processing.
#:	Indicates the number of the reaction. The numbers are assigned as the reactions are read from the reaction set. These numbers correspond to the reaction numbers assigned in the reactuse file.
Reactions:	The reactions are sorted by rates from the largest to the smallest.
Rate:	In the preprocessor mode, the rate is the calculated rate coefficient. In the post-processor mode, it is rate coefficient multiplied by reactant concentrations.

The module is repetitive so that various times may be examined without redefining the species of interest. To exit Preliminary screening type -1 at "Enter time". It is not necessary to exit to examine a different species but it is necessary to exit to examine a different ARCHON index run.,

SECTION 5
ARCHON STANDARD REACTION SET - ARD_5

The "standard" ARCHON reaction rate data set is now called ARD_5.set and has been significantly updated from prior versions. It now consists of over 9000 reactions involving over 400 species. Several corrections have been made to the original ARCHON file and significant additions have been made in electron impact dissociation and ionization and in nitrogen electronic excitation to, and relaxation from the "A", "B" and "C" states of the neutral and to the "A" and "B" states of the ion. Additions have also been made in the area of negative ion and electron-impact reaction rates. However, *the user is cautioned* that in the area of negative ion chemistry, there is considerable uncertainty in the rates since there is a paucity of specific rate measurements on the topic. The reaction rate data set is heavily commented and should be treated as "experimental" in the sense that it is undergoing constant updates and revisions. Comments and suggestions for the reaction rate data set are welcome.

Because the reaction set is so large, it is distributed on "floppy" disk only and is not printed out for "hardcopy" documentation as a standard report. The following is the "header" information from the ARD_5 data set.

ARCHON D5

ARCHON-D5 is the ARCHON database used for low temperature and high temperature modeling of the atmosphere.

A descriptive syntax is employed for reactions and rate coefficients which was designed to promote use of the data base as a reference resource as well as compatibility with the ARCHON code architecture. Names of the species were chosen to accurately reflect their chemical nature as well as to conform to the spirit of the ARCHON architecture. Each reaction in a sub-section will be headed by an "*" with the number of the section following. If the reaction is a high temperature reaction an "h" will follow the number of the section. Within each sub-section the order of reactions, as well as the species in a reaction, follows a set of rules. These rules exist only to facilitate the analyst or kineticist in using the data base and are not critical for use of the databases by ARCHON.

The rules are as follows:

- Within a reaction, atoms are listed first, except in subsections involving ions, where the ion is listed first.
- Atoms are first ordered alphabetically and then ordered from the ground state through excited states.
- Molecules (and multi-atom free radicals) are first ordered by size, secondarily ordered alphabetically, and finally sorted through their excited states.

- Reactants e and M are listed last.
- Within a sub-section, the list of reactions is then sorted by the first reactant, also using the above set of rules, In the case where the first reactants are the same, the reactions are sorted by the second reactant. If further organization is required, then sorting is done on the next species listed in the reaction.

The format used for numerical characterization of rate coefficient data is based upon the convention used in the DNA Handbook, supplemented as follows:

R1 + R2 + R3 ---> P1 + P2 + ... + P8 A B C D E [T1<T<T2] |USRSUB

Where A is positive, the A, B, C, D, and E will be used to from the DSWA standard form for the temperature-dependent rate coefficient:

$$k(T) = A*(T/300)**B*EXP[-1000*C/T**(1/D)]; \quad (5.1)$$

If E is specified, it is kinf, and the k(T) is modified to account for third body saturation

$$keff(t) = k(T)*M/(1+k(T)*M/kinf)*0.6**[1/(1+(log10(k(T)*M/kinf)**2)] \quad (5.2)$$

If A is negative then an alternative power series will be used instead:
*

$$k(T) = (-A + B*T**2 + C*T**3 + D*T**4) * EXP(-1000*E/T) \quad (5.3)$$

If the rate coefficient data is not tractable with either of these three forms then the user may supply a subroutine USRSUB. The symbol "|" is employed to indicate that a call to a user-supplied subroutine is required to calculate the rate coefficient for that reaction. The name, up to 16 characters, following the USRSUB symbol should be the name of the subroutine that the user supplies and compiles into the RATE.FOR package supplied in the ARCHON code. The user must edit RATES.FOR such that the SURSUB is present, and that the arguments match in number and type between the call and the subroutine.

ARD_5 Table of Contents

9. Three-Body Attachment
10. Collisional Detachment
11. Dissociative Attachment
12. Associative Detachment
13. Positive-Ion Charge Transfer
14. Positive Ion-Atom Interchange
15. Negative-Ion Charge Transfer
16. Negative Ion-Atom Interchange
18. Positive-Ion Photodissociation
19. Three-Body Positive-Ion-Neutral Association
20. Positive-Ion Collisional Dissociation
22. Negative-Ion Photodissociation
23. Three-Body Negative-Ion-Neutral Association
24. Negative-Ion Collisional Dissociation
25. Radiation-Stabilized Neutral Recombination
26. Neutral Photodissociation
27 Three-Body Neutral Recombination
28. Neutral Collisional Dissociation
29. Neutral Rearrangement
30. Radiative Electronic-State Deexcitation
31. Electronic State Photoexcitation
32. Collisional Electronic-State Quenching
32r. Reverse of Category 32
33. Vibrational state radiative relaxation and photo-excitation
34. Collisional Vibrational State Quenching
35. Collisional Vibrational Energy Exchange
C. Carbon Chemistry
U. Uranium Chemistry
Al. Aluminum Chemistry
SuppA. Supplement A (ion-ion recombination)
SuppB. Supplement B (beta

APPENDIX A
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